

On the Constitution of Tea Tannin

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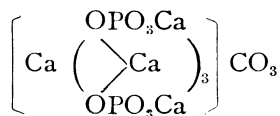
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But the contents of calcium seemed to be inconstant. The author therefore expected, these variations must be caused by the different combination of bone-protein. And the author prepared collagen from bone and examined first its amino acid contents.

Preparation of collagen

The bones were removed from the body immediately after death. The adherent soft tissues were dissected and steeped in 0.1~0.2% HCl about 2~3 days. And then washed with distilled water and steeped into 0.1~0.2% NaOH and washed with distilled water, then dried with alcohol and ether. The contents of amino acid of these samples were determined by Van-Slyk's method.

The results showed that the contents of arginine are higher in male than in female.

On the Constitution of Tea Tannin.⁽¹⁾

By

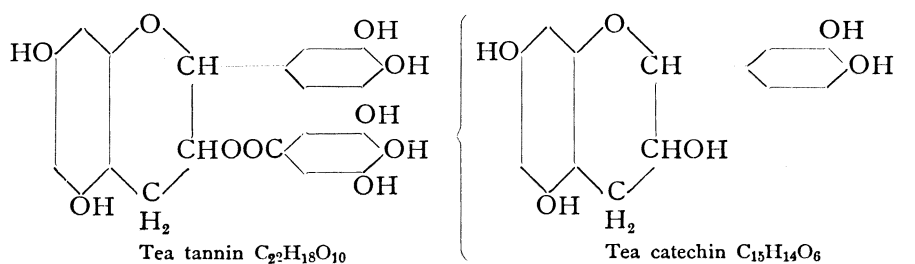
Michiyo TSUJIMURA.

(Received March 9 th, 1931.)

In the previous report, it was stated that tea tannin, isolated by the author from green tea, is most probably the gallic acid ester of tea catechin⁽²⁾ represented by the following formula :

(1) M. Tsujimura: Bull. Agricult. Chem. Soc. Japan, **6**, 62 (1930).

(2) " : " " " **6**, 70 (1930).

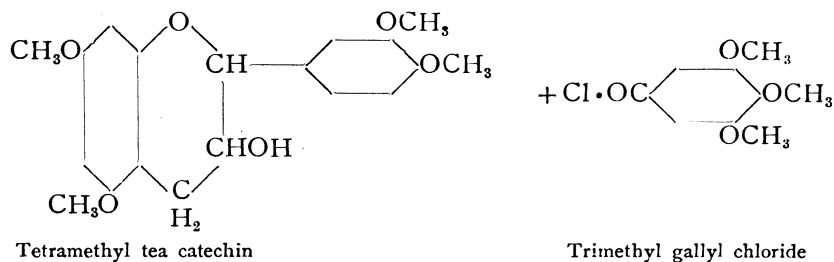


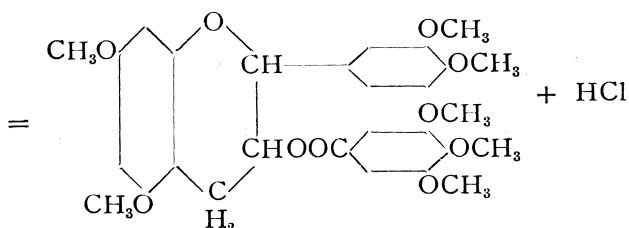
On acetylation, tea tannin forms heptaacetyl derivative corresponding to the formula, $C_{22}H_{11}O_{10}(COCH_3)_7$, and by boiling with 5% sulphuric acid it gives gallic acid and a reddish brown substance which yields phloroglucinol when heated with 50% potash. Unfortunately, tea catechin could not be detected among the hydrolytic products, because the latter easily changes to a reddish brown substance when heated with sulphuric acid.

Continuing the studies on this subject, the author has now prepared a methyl derivative and proved it to be heptamethyl tea tannin $C_{22}H_{11}O_3(OCH_3)_7$

By oxidative decomposition with potassium permanganate, this compound gives trimethyl gallic acid $(OCH_3)_3C_6H_2CO_2H$ and veratric acid $(OCH_3)_2C_6H_3CO_2H$.

Although these facts are in accordance with the above assumption, yet more decisive proof must be forwarded by means of the direct synthesis of this compound, and so the author attained this by preparing heptamethyl tea tannin synthetically. For this purpose, tetramethyl tea catechin was coupled with the chloride of trimethyl gallic acid in presence of quinoline, according to the following scheme :





Tetramethyl tea catechin-trimethyl galloate (Heptamethyl tea tannin)

The reaction proceeded smoothly and tetramethyl tea catechin trimethyl galloate $C_{22}H_{11}O_3(OCH_3)_7$, was obtained as colourless prisms or plates, melting at 140° . It shows no optical activity. The absorption spectrum of this compound (Fig. 3) was found to be identical with that of heptamethyl tea tannin (Fig. 4) prepared from natural tea tannin, while that of tetramethyl tea catechin (Fig. 1) or of trimethyl gallic acid (Fig. 2) was quite different from that of the latter (Fig. 4). The synthetical product when demethylated, forms an amorphous white powder which gradually oxidizes in the air to a reddish mass just like the natural tea tannin. Thus the author believes that the constitutional formula of tea tannin above stated is fully confirmed.

Experimental.

1. Methylation of Tea Tannin.

1.4 grams freshly prepared tea tannin were dissolved in 6 c.c. methyl alcohol, to which 5 c.c. dimethyl sulphate were added and treated with 5 c.c. 50% KOH drop by drop with shaking. The reaction product was poured into water, and after standing for an hour it was collected, washed with water and dried on a porous tile; the yield was ca. 1.4 grams. For purification it was dissolved in acetone, treated with a little animal charcoal, filtered and evaporated; the residue thus obtained was again dissolved in hot methyl alcohol, and the substance separated on cooling were dried first on a porous tile and afterwards in a desiccator containing conc. sulphuric acid.

The analysis gave following result:

	Sample	CO ₂	H ₂ O	C%	H%
I.	3.178 mg.	7.335 mg.	1.769 mg.	62.95	6.19
II.	2.463 "	5.722 "	1.330 "	63.36	6.00
	average			63.16	6.10
	calc. for $C_{22}H_{11}O_3(OCH_3)_7 + \frac{1}{2}H_2O$			63.40	6.06

Thus the analysis proved it to be heptamethyl tea tannin.

Specific rotation of this compound in acetone solution: $[\alpha]_D^{19} = -135^\circ$.

2. Oxidation of Heptamethyl Tea Tannin with Potassium Permanganate.

The oxidation was carried out according to the method of Perkin⁽³⁾ as follows :

(1) Heptamethyl tea tannin was dissolved in methyl alcohol, heated on a water bath and a strong solution of potassium permanganate was added drop by drop until the red colour remained unchanged on standing. The excess of permanganate was then decomposed with sodium sulphite and filtered; the filtrate was neutralized with dilute sulphuric acid and extracted with ether. The ethereal extract was evaporated and the crystalline residue thus obtained was treated with sodium bicarbonate to remove the phenolic substance and recrystallized from hot water. Trimethyl gallic acid was thus obtained as colourless needles melting at 167°.

The analysis gave the following result :

Sample	CO ₂	H ₂ O	C%	H%
2.776 mg.	5.743 mg.	1.483 mg.	56.43	5.93
calc. for trimethyl gallic acid (CH ₃ O) ₃ C ₆ H ₂ CO ₂ H			56.58	5.70

(2) 1.7 grams heptamethyl tea tannin were mixed with water and oxidized with permanganate in the same way as above-mentioned; the operation lasted for 30 hours. The crystals obtained thereby consisted of trimethyl gallic acid and veratric acid. The latter acid isolated from the mixture melted at 175°. Mixed with pure preparation of veratric acid, no depression of melting point was observed.

3. Isolation of Tea Catechin.

For the isolation of tea catechin, the method⁽²⁾ previously mentioned was somewhat modified as follows :

The hot water extract of green tea (inferior quality) was treated with so much neutral lead acetate until no more precipitate was formed. The thick precipitate thus produced was filtered off, and the clear filtrate was treated with dilute caustic soda until faintly alkaline reaction was noticed. The yellow precipitate formed thereby was collected, washed with water and decomposed with hydrogen sulphide. The filtrate from lead sulphide was evaporated in vacuum to a small volume and repeatedly shaken with ethyl acetate. The united ethyl acetate extract was evaporated and the residue therefrom was dissolved in hot water and filtered while hot. From the filtrate tea catechin crystallized out on cooling, which after recrystallization

(3) A. G. Perkin: Soc., **87** 398, (1905).

Tetramethyl tea catechin $\frac{1}{1000}$ mol.

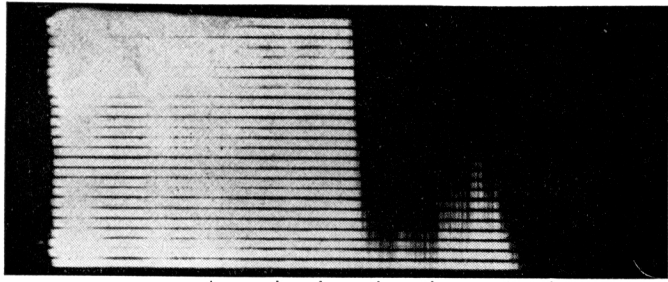


Fig. 1.

Trimethyl gallic acid $\frac{1}{5000}$ mol.

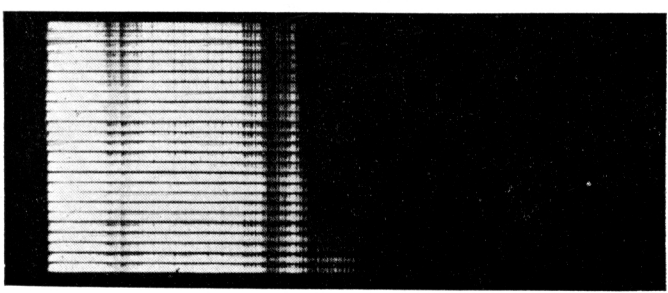


Fig. 2.

Tetramethyl tea catechin-trimethyl galloate $\frac{1}{20000}$ mol.

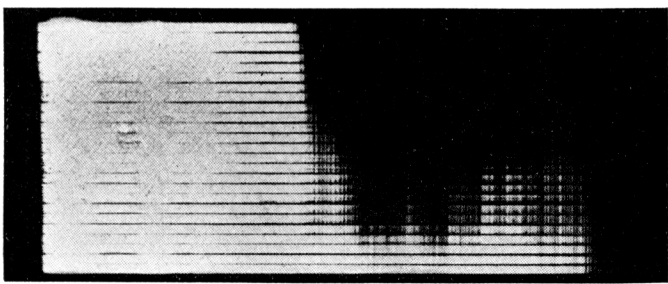


Fig. 3.

Heptamethyl tea tannin $\frac{1}{10000}$ mol.

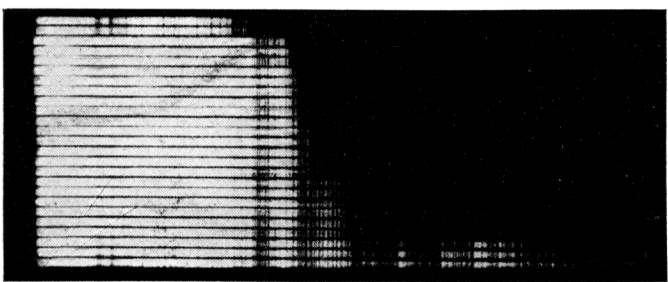


Fig. 4.

melted at 237~238°. The yield was ca. 0.11% of the green tea used.

4. *Tetramethyl tea catechin.*

The methylation of tea catechin was carried out as previously mentioned.⁽⁴⁾ Tetramethyl tea catechin thus obtained melted at 153~154°.

5. *Trimethyl gallic acid.*

The methylation of gallic acid was also carried out in the same manner as in the case of tea catechin. The methylated product was poured into water and warmed on a water bath at 60° for three hours. After cooling it was acidified with sulphuric acid, whereby the crystals of trimethyl gallic acid separated out, which was washed with water and dried on a porous tile; m. p. 167°. Mixed with trimethyl gallic acid obtained by the hydrolysis of heptamethyl tea tannin, it gave no depression of melting point.

6. *Trimethyl Gallyl Chloride.*

2 grams thionyl chloride were mixed with 0.5 gram trimethyl gallic acid in a glass tube, and warmed in a water bath. When the reaction was ended, the excess of thionyl chloride was removed by distillation in vacuum and the tube was immediately sealed.

7. *The Synthesis of Tetramethyl Tea Catechin-Trimethyl Galloate.*

The synthesis was carried out according to the method of E. Fischer.⁽⁵⁾ For this purpose 0.4 gram tetramethyl tea catechin and 0.5 gram trimethyl gallyl chloride were dissolved in 2 c.c. of chloroform. 1 cubic cm. quinoline was added to it and the mixture was shaken for an hour. After standing for three hours, it was diluted with chloroform, and washed with dilute sulphuric acid and water successively. The chloroform solution was then evaporated under reduced pressure, the residue therefrom was dissolved in hot methyl alcohol and filtered while hot. After standing for some time, the crystals separated out, which after recrystallization formed colourless prisms or plates, melting at 140°.

The analysis gave following result :

	Sample	CO ₂	H ₂ O	C%	H%
I.	3.296 mg.	7.793 mg.	1.825 mg.	64.48	6.15
II.	2.299 "	5.465 "	1.245 "	64.98	6.16
			average	64.73	6.16
calc	for tetramethyl tea catechin-trimethyl galloate	C ₂₂ H ₁₁ O ₃ (OCH ₃) ₇		64.41	5.97

(4) loc. cit.

(5) E. Fischer und M. Bergmann: B, 15, 1760, (1918).

The crystals dissolved in acetone showed no optical rotation.

The author expresses her sincere thanks to Prof. U. Suzuki for his kind direction throughout this work.

On the Isolation of Phytosterolin from Wheat Embryo.

By

Nobuzo NAKAMURA and Akiyoshi ICHIBA.

(Received March 9th, 1931.)

In the course of studying on the ether extract of wheat embryo,* we came to isolate a glucosidic substance, which we believed to be phytosterolin as designated first by F. B. Power and A. H. Salway and certified by them of natural occurrence.⁽¹⁾

For the preparation, air dried wheat embryo powder was extracted exhaustively with ether. The oil obtained was perfectly clear at first, but after several days gave a small quantity separating out. It was collected and washed with hot ether and ethyl alcohol. This insoluble material was dissolved in a small amount of hot amyle alcohol. On standing, microscopic needle crystals were obtained; m. p. 285°~290°C (uncorr.), yield 0.2%.

Acetate: m. p. 168°C (uncorr.), $[\alpha]_D = -22.4^\circ$ (in chloroform).

Benzoate: m. p. 198°C (uncorr.), $[\alpha]_D = +17.24^\circ$ (in chloroform).

On hydrolyzing, phytosterol with melting point 137°C (uncorr.) and glucose were obtained. The details were as follows:

Experimental.

In order to ascertain a pure material, the crude material thus obtained was acetylated with acetic anhydride, which was then recrystallized from ethyl alcohol in colourless, glistening leaflets, melting at 168°C (uncorr.).

The acetate was converted again into original state by saponifying and washing with water, alcohol, and ether.

Liebermann-Burchard's and Hager-Salkowski's reactions for sterols, as well as α -Naphthol reaction for carbohydrates were positive.

* Not extra pure, but contaminated with bran.

(1) J. Chem. Soc., 103 (1913), 339, 1022.